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Phase quantification in cementitious materials by dynamic modulus mapping

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ABSTRACT

Understanding mechanism at the microscale level is essential for tailoring cementitious material to achieve better concrete and structure performance. To identify the distinct microstructural features and to provide insight into the mechanism by which the phases in hardened paste possess, this study adopts the technique of quantitative modulus mapping in the form of Scanning Probe Microscopy (SPM) images to characterize non-destructively the hardened ordinary Portland cement (OPC) paste and slag-blended cement paste at the microscale level. It is found that SPM modulus mapping is capable of identifying individual phase based on the local variation of nanomechanical properties. A method is proposed to quantify the size of the identified phase, especially the thickness of the inner C-S-H layer. With the facilitation of SPM mapping image, the indent location can be located to recognize in which phase the nanoindentation has been made. The results indicate the significance of SPM-based modulus mapping technique as a powerful tool for fundamental study of the cementitious materials with more attractive features of higher spatial resolution to quantify the phase size in nanometer scale level under a nondestructive testing condition.

1. Introduction

Concrete is a multi-phase and multi-scale material. Many macroscopic behaviors of concrete originate from the nano-scale properties of individual phases. It is a fundamental requirement to understand the mechanism at the nano-scale level for further material tailoring to achieve better conrete.

Quantitative modulus mapping in the form of Scanning Probe Microscopy (SPM) technique has been found more appropriate than the static nanoindentation for characterizing multi-phase or composite materials [1–3]. The quantitative modulus mapping and nanoindentation can be measured using the same equipment but under different operating model. Similar to static nanoindentation, modulus mapping is a nanomechanical probe-based method but characterized as a nondestructive test with contact stiffness of materials measured at a much smaller contact force than that used in nanoindentation. This modulus mapping technique with in situ SPM imaging has been widely used to characterize the frequency response of polymer materials [4–5]. In recent years, it has been used to evaluate the microstructural features and viscoelastic behavior of solid, such as human teech [2,6]. The application of SPM-based modulus mapping technique to cementitious materials is found scarce [7–8]. Its powerful functions have not been fully explored for characterizing cementitious materials with multi-scale and multi-phase features.

To identify the distinct microstructural properties and provide insight into the mechanism by which the phases in hardened paste possess, this study utilizes Scanning Probe Microscopy (SPM) to characterize ordinary Portland cement (OPC) and slag-blended cement pastes at the microscale. The following has been investigated: modulus mapping-based microstructure morphology of OPC and slag-blended cement pastes; thickness of inner product (IP) layer surrounding different types of grains; the indentation modulus of individual phase measured with the facilitation of modulus mapping image.

2. Methods

2.1. SPM Technique

Quantitative modulus mapping in the form of Scanning Probe Microscopy (SPM) images was conducted using the direct force modulation operating model of a Tribo nanoindenter (Hysitron) equipped with Berkovitch tip (Fig. 1a). SPM is a general term for various probes that are used for imaging and measuring surfaces on a fine scale. This technique is capable of mapping the local variation of nanomechanical properties without causing plastic deformation to the material [2]. The

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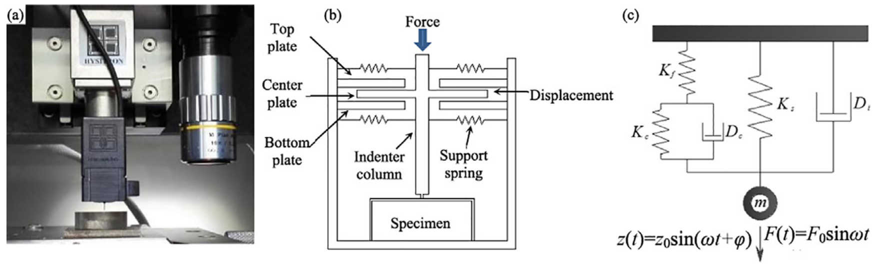

Fig. 1. (a) Equipment mounted with a Berkovich intent tip and microscope, (b) schematic illustration of mechanism and (c) physical model of SPM measuring system.

contact stiffness can be directly obtained continuously forming a modulus mapping, which is ideal for multiphase and composite materials. A quasi-static force of 4 μN (dc force) was superimposed by a 3.5 μN sinusoidal force (ac force) at a frequency of 200 Hz in this study. A Lock-in amplifier was utilized to analyze the sample response, the displacement amplitude and the phase shift between the ac force and the displacement can be obtained (Fig. 1b). The contact stiffness and the material damping were calculated from the amplitude and the phase shift [1–2].

This testing system can be modeled as a physical system with force applied to a mass that is attached to the two fixed Voigt elements (Fig. 1c). The two elements represent the stiffness and damping of the transducer and the contact, respectively. The model yields a differential equation describing the relationship between the applied force and the motion:

$$F(t) = F_0 \sin(\omega t) = m\left(\frac{d^2z}{dt^2}\right) + D\left(\frac{dz}{dt}\right) + Kz \quad (1)$$

where, F_0 is the amplitude of the applied sinusoidal force, m is the mass of the transducer, ω is the angular frequency, z is the sinusoidal displacement response, $D = D_i + D_c$ is the combined damping coefficient of system and the contact, $K = K_s + K_c$ is the combined stiffness of the spring and the contact, K_f is the stiffness of the system frame, which is much greater than that of the contact and thus can be neglected. The solution to Eq. (1) is:

$$z = z_0 \sin(\omega t + \varphi) \quad (2)$$

$$z_0 = \frac{F_0}{\left[(K - m\omega^2)^2 + (D\omega)^2\right]^{\frac{1}{2}}} \quad (3)$$

where, φ is the phase of the displacement, $\tan(\varphi) = -\frac{D\omega}{K - m\omega^2}$.

The storage modulus (E') and the loss modulus (E'') of the contact can be calculated as:

$$E' = \frac{K_c}{2a} \quad (4)$$

$$E'' = \frac{\omega D_c}{2a} \quad (5)$$

$$a = \sqrt{\frac{3FR}{2K_c}} \quad (6)$$

where, F is the contact force, R is the tip radius of indenter, which is determined as 400 nm by standard nanoindentation protocol in this study. Storage modulus represents the material capacity to store energy, large storage modulus means greater elastic property of material. Loss modulus represents the material capacity to dissipate energy as heat, and large loss modulus represents more viscoelastic. They are generally used to characterize the viscoelastic response of a material.

2.2. Nanoindentation Test

The quasi-static force modulation of Tribo nanoindenter (Hysitron) was used for the discrete nanoindentation test to obtain the indentation modulus and hardness of each indents made on the individual phase. The loading pattern was set as first loading to a maximum load of 2 mN within 10 s followed by a holding period of 5 s at the maximum load, and then it was unloaded within 10 s to zero load. By analyzing the initial part of the unloading curve, the indentation modulus M and hardness H can be obtained as [9]:

$$M = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A_c}} \quad (7)$$

$$H = \frac{P_{max}}{A_c} \quad (8)$$

where, $S = \left(\frac{dP}{dh}\right)_{h = h_{max}}$ is the contact stiffness and determined from the slope of the initial part of the unloading curve; h_{max} is the maximum indentation depth; β is the geometrical correction factor, for the Berkovich tip used in this study, $\beta = 1.034$; P_{max} is the maximum load; A_c is the projected area of contact, it is a function of the equivalent half cone angel $\theta_{eq} = 70.32°$ and the contact depth h_c:

$$A_c = \pi \cdot (\tan\theta_{eq} \cdot h_c)^2 \quad (9)$$

$$\frac{h_c}{h_{max}} = 1 - 0.75\frac{P_{max}}{Sh_{max}} \quad (10)$$

2.3. Sample Preparation

Ordinary Portland cement (OPC) and slag cement were used as cementitious materials. The chemical composition in terms of oxide mass percentage and the physical properties of each material are listed in Table 1. Two types of pastes are investigated: OPC paste (denoted as O) vs. slag-blended paste (denoted as S). In slag-blended paste, the OPC was replaced by slag at the level of 50% by mass of the total cementitious materials. The water/cementitious (w/cm) ratio of the pastes is 0.3. After mixing, the fresh paste was filled into a plastic tube with diameter of

Table 1
Chemical compositions and physical properties of cementitious materials.

Materials	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	Ignition loss (%)	Specific gravity	Blaine fineness (cm^2/g)
Portland cement	20.55	4.59	3.27	62.5	2.61	2.93	0.53	0.83	1.77	3.14	3500
Slag	34.55	14.36	0.45	33.94	11.16	1.94	0.26	0.56	0.7	2.88	3820